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Sludge: A waste or renewable source for energy and resources recovery?

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ABSTRACT

Utilization of waste sludge as a renewable resource for energy recovery is the appropriate solution of how to manage the continuously increasing waste sludge generation effectively in order to meet stringent environmental quality standards, and at the same time, how to sustain the supply of reliable and affordable energy for our future generations and ourselves. The valuable characteristics of sludge, including high energy and nutrient content, with the stringent criteria of sludge disposal, driving the environmental engineers and scientist to change their standpoint to considering sludge as a viable resource of energy instead of a waste. It may be an important move towards the development of a sustainable energy solution to fulfill present and future energy requirements and thus reduce the dependency on non-renewable resource. Thus, this review discusses about the type of resources that can be recovered from waste sludge and, conventional and emerging methods used to convert the sludge into valuable resources. Moreover, the major factors involved in the process, stage of application, advantages and possible drawbacks of the methods are also discussed.

Contents

Abbreviations: AD, anaerobic digestion; ALWA, artificial lightweight aggregate; AOP, advanced oxidation process; BNR, biological nutrient removal; Bt, *Bacillus thuringiensis*; C/N, carbon to nitrogen ratio; CHP, combined heat and power; DO, dissolved oxygen; DS, dry solids; FFA, free fatty acids; HPH, high pressure homogenizer; HRT, hydraulic retention time; kWh, kilowatt per hour; LHV, low heating value; MFC, microbial fuel cells; mgd, million gallon/day; MPa, megapascal; MT, metric ton; MW, megawatt; MW, microwave; MWh, megawatt per hour; NACWA O&M, National Association of Clean Water Agencies Operation and Maintenance; OLR, organic loading rate; p.e., population equivalent; PAH, polycyclic aromatic hydrocarbons; PAO, polyphosphate accumulating organisms; PCB, polychlorinated biphenyls; PCB, printed circuit board; PHA, polyhydroxyalkanoates; PHB, poly-β-hydroxybutyric acid; SCOD, soluble chemical oxygen demand; SCWO, supercritical water oxidation; SRT, sludge retention time; SS, suspended solids; STORS, sludge to oil reaction system; TCOD, total chemical oxygen demand; TKN, total kjeldahl nitrogen; TOC, total organic carbon; TP, total phosphorus; TS, total solids; UASB, up-flow anaerobic sludge blanket; USEPA, United States Environmental Protection Agency; VFA, volatile fatty acids; VS, volatile solids; VSS, volatile suspended solids; w/v, weight by volume; w/w, weight by weight; WAO, wet air oxidation; WAS, waste activated sludge; WWTP, wastewater treatment plant

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1. Introduction

The growing global urbanization of society coupled with increasingly stringent sludge reuse/disposal regulations and increasing public pressure, is forcing both public and private sludge generators to re-evaluate their sludge management strategies [1]. Conventionally, the waste sludge is disposed via incineration, landfilling or ocean disposal as well as reused as soil conditioner in agriculture. With the recent banning of ocean disposal and new stringent European landfilling criteria, much more sludge is now beneficially reused, both in agriculture and via a variety of thermal technologies [2]. The selection of a sludge management strategy is of interest to a wide variety of groups including facility owners, engineering consultants, contract operators, equipment suppliers, politicians, regulators, environmental groups and the general public. Selection of a sludge management strategy based on the actual needs of the community rather than on some artificial set of criteria is probably the single most important component in achieving long-term sustainability [3]. It is anticipated that upcoming sludge management efforts will accentuate upon the recovery and reuse of value added crops from sludge [4]. This interest in renewable energy has been driven by a combination of shrinking reserve of fossil fuels due to rising demand for primary energy, fuel price spikes, climate change concerns, public awareness, and advancements in renewable energy technologies [5,6].

The two components in sludge that are technically and economically feasible to recycle are nutrients (primarily nitrogen and phosphorus) and energy (carbon) [3]. There are several options available for energy recovery from waste sludge. The utmost significant routes are anaerobic digestion of sludge with biogas recovery, co-digestion, incineration and co-incineration with energy recovery, pyrolysis, gasification, supercritical (wet) oxidation, use in the production of construction materials, production of bio-fuels (hydrogen, syngas, bio-oil), electricity generation by using specific microbes, and beneficial recovery of heavy metals, nutrient (nitrogen and phosphorus), protein and enzymes. Thus the present efforts are aimed to provide an overview, and discuss the ways to achieve more sustainable sludge management strategy by recovering the energy rich products.

2. Sludge characterization

Sewage sludge is a complex heterogeneous mixture of microorganisms, undigested organics such as paper, plant residues, oils, or fecal material, inorganic materials and moisture [7]. The undigested organic materials contain a highly complex mixture of molecules coming from proteins and peptides, lipids, polysaccharides, plant macromolecules with phenolic structures (e.g. lignins or tannins) or aliphatic structures (e.g. cutins or suberins), along with organic micro-pollutants such as polycyclic aromatic hydrocarbons (PAH) or dibenzofurans [8]. Table 1 depicts the characteristics of primary and secondary activated sludge.

Table 1
Characteristics of primary sludge and activated sludge [10].

Parameter	Primary sludge	Activated sludge	Composition
Total dry solids (total solids, TS) %	5–9	0.8–1.2	• Non-toxic organic carbon compounds (appx. 60% on dry basis), Kjeldhal-N, phosphorus containing components.
Volatile solids, VS (%TS)	60–80	59–68	• Toxic pollutants: heavy metals (Zn, Pb, Cu, Cr, Ni, Cd, Hg, As: Concentration vary from 1000 mg/L to less than 1 mg/L), polychlorinated biphenyls (PCB), PAH, Dioxins, Pesticides, Endocrine disrupters, Nonyl-phenols.
Nitrogen (%TS)	1.5–4	2.4–5.0	• Pathogens and other microbiological pollutants.
Phosphorus (%TS)	0.8–2.8	0.5–0.7	• Inorganic Compounds: Silicates, aluminates, calcium and magnesium containing compounds.
Potash (K_2O %TS)	0–1	0.5–0.7	• Water, varying from a few percent to more than 95%.
Cellulose (%TS)	8–15	7–9.7	
Iron (Fe g/kg)	2–4	–	
Silica (SiO_2%TS)	15–20	–	
pH	5.0–8.0	6.5–8.0	
Grease and fats (%TS)	7–35	5–12	
Protein (%TS)	20–30	32–41	
Alkalinity (mg/L as $CaCO_3$)	500–1500	580–1100	
Organic acids (mg/L as acetate)	200–2000	1100–1700	
Energy content (kJ/kg TS)	23,000–2900	19,000–23,000	

Primary sewage sludge is generated through mechanical (screening, grit removal, sedimentation) wastewater treatment process, usually contains from 93% to 99.5% water, high ration of suspended and dissolved organic matters. Waste activated sludge (WAS) or secondary sludge, is generated during biological treatment of the wastewater, and contains mainly microbial cells that are complex polymeric organic materials. The total solids concentration in secondary sludge ranges between 0.8% and 1.2%, which also depends on the type of biological treatment process employed [9].

Waste activated sludge is consisted 59–88% (w/v) of organic matter, which is decomposable and produces the offensive odors. Only a small part of the sludge is solid matter in which over 95% is water. The organic portion contains 50–55% carbon, 25–30% oxygen, 10–15% nitrogen, 6–10% hydrogen, 1–3% phosphorus and 0.5–1.5% sulfur [11]. The ash from waste sludge contains mainly minerals such as quartz, calcite or microline. These minerals are formed by elements such as Fe, Ca, K and Mg. Furthermore, some heavy metals such as Cr, Ni, Cu, Zn, Pb, Cd and Hg can also be found in the sludge [12].

The potential for energy recovery from sludge is a function of their composition, which is a mixture of organic (volatile) matter, inorganic matter (inert material) and associated water. The energy content of sludge is laid in the volatile solids, which is subdivided into two components: readily degradable (50% in primary sludge and 25% in WAS) and not readily degradable (30% in primary sludge and 55% in WAS) [6].

3. Techniques for resource recovery

The conventional and emerging methods for resource recovery from sludge are:

1. Anaerobic digestion
3. Incineration and co-incineration
3. Gasification
4. Pyrolysis
5. Wet air oxidation
6. Supercritical wet oxidation
7. Hydrothermal treatment

There are many sludge derived resource recovery options including recovery of biogas, fuel gas, electricity generation, production of construction material, nutrient recovery, biofuel recovery (syngas, bio-diesel, bio-oil), recovery of hydrolytic enzymes, polyhydroxyalkanoates (PHA) (for bio-plastic manufacturing), bio-fertilizers, bio-sorbents etc. using abovementioned treatment methods. Fig. 1 also shows the routes of resources recovery from waste sludge.

3.1. Anaerobic digestion (AD)

Anaerobic digestion is the most popular sludge stabilization technology currently in the market [5]. The process transforms sludge organic solids to biogas, which is a mixture of CH_4, CO_2, and traces of other gases, in an anaerobic environment (Reaction 1) [9].

$$\begin{aligned} &C_cH_hO_oN_nS_s + yH_2O \rightarrow xCH_4 + nNH_3 + xH_2S + (c-x)CO_2 \\ &x = 1/8(4c + h - 2o - 3n - 2s) \\ &y = 1/4(4c + h - 2o + 3n + 3s) \end{aligned} \tag{1}$$

This conversion is a complex process involving four phases of biochemical reactions. These phases are hydrolysis in which organic compounds (polysaccharides, proteins, and fat) are hydrolyzed by extracellular enzymes; acidogenesis, in which the products of the hydrolysis are converted into hydrogen, formate, acetate, and higher molecular-weight volatile fatty acids (VFA); acetogenesis, where short-chain organic acids and alcohols produced by acidogenesis are further processed by acetate-forming bacteria to yield mainly acetic acid, as well as carbon dioxide and hydrogen; and methanogenesis, in which biogas (methane and carbon dioxide) is produced from hydrogen, formate, and acetate [13]. This biogas can be utilized as a source of energy in the production of electricity and/or heat.

3.2. Incineration and co-incineration

The main purpose of sludge incineration is the complete oxidation of the organic compounds at high temperature. In this process, the biosolids are burned in a combustion chamber supplied with excess air (oxygen) to form mainly carbon dioxide and water, leaving only inert material (ash). This ash has to be disposed of or can be used as a source for the production of building materials. Presently, sludge incineration methods are progressively determined on the energy recovery from the sludge in the form of heat or electricity [14]. According to National Association of Clean Water Agencies (NACWA) [6], incineration with power generation has been successfully implemented by the Metro wastewater treatment plant (WWTP) in St. Paul, Minnesota, United States (U.S.). The plant has a 3.5 MW generation capacity, which reportedly reduces the plant's greenhouse gas emissions by approximately 18%. A number of other incineration facilities in Cleveland, Ohio (U.S.) and in Hartford, Connecticut (U.S.) are in

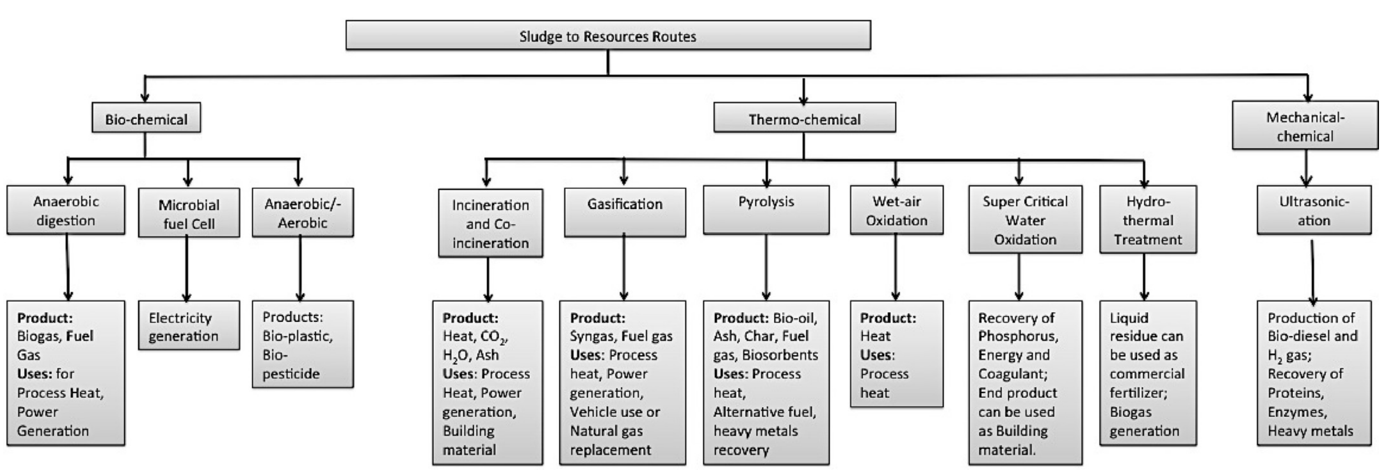

Fig. 1. Routes of resource recovery from waste sludge.

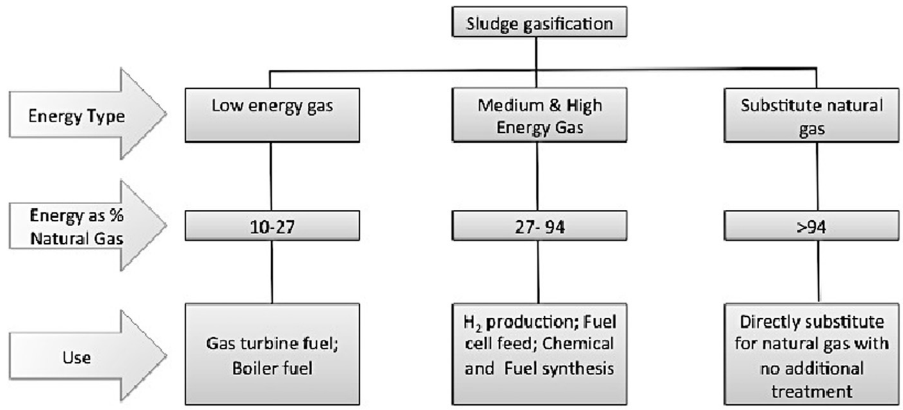

Fig. 2. Gases generated during gasification and their potential uses [6].

design to implement power recovery with expected generation capacities of 2.0 and 0.8 MW, which will provide 20% and 40% of the facilities' energy needs, respectively.

In order to preclude the high costs of an incineration plant for sludge as well as to advance the energy retrieval efficacy, options have been explored to incinerate dried sludge in a coal-fired power plant [15]. The energy recovery from sludge incineration can effectively be enhanced by enhancement of the sludge dewatering and drying processes and possibly also by the usage of the low-caloric surplus heat from the exhaust gases of the power plant [4].

3.3. Gasification

Gasification involves the breakdown of dried sludge in an ash and in combustible gases at temperatures usually about 1000 °C in an atmosphere with a reduced amount of oxygen [16]. The products of the process include heat (utilized to generate power and process heat) and syngas (synthetic gas). The chemical composition of the end products and the energy content are affected by the gasification agent (air, oxygen, or steam), the gasifier operating temperature and pressure, and feed characteristics (type, dry solids, and volatile solids). Fig. 2 showing the gases generated during gasification, their energy efficiency and potential uses. Dry material, such as wood or green waste, can be mixed with the sludge to meet the required energy characteristics.

Biosolids gasification is expected to result in significant energy recovery, but these types of systems are still in the early stages of implementation and will need to be proven over time. An advanced pressurized entrained flow gasifier has been started at pilot scale in Germany. Gasification takes place at high temperature (1400–1700 °C) and high pressure (0.6–2.6 megapascal (MPa)), using pure oxygen as the oxidant. At these high temperatures, the ash from the sludge forms a molten slag, which is quenched, in the bottom of the gasifier, forming fine-grained slag particles. The raw gas is cleaned by removing CN, NH_3 and H_2S to produce a high quality syngas. The vitrified slag is completely inert and can be used as an ingredient in concrete mixes. Extensive monitoring of the process has revealed that heavy metals and organo-chlorine compounds are completely controlled [17].

3.4. Pyrolysis

Sludge pyrolysis is an innovative method developed to manage sludge and energy, wherein the sludge is thermally treated (350–500 °C) under pressure and in the oxygen deficient environment [18]. In this method, the sludge is transformed into char, ash, pyrolysis oils, water vapor, and combustible gases. Portion of the solid and/or gaseous products of the pyrolysis method are incinerated and used as heating source in the pyrolysis process. Process temperature, reaction time, operating pressure and raw materials' characteristics are the main factors that affect the yields of pyrolysis products [19]. Fluid beds are the most popular configurations of pyrolysis due to their ease of operation and ready scale-up, thus they are commercially popular nowadays [20]. A commercial installation of the pyrolysis process (SlurryCarb™, California, U.S.) is operating at a temperature of about 450 °C. The pyrolysis reaction alters the molecular structure of the solids and releases CO_2, thus reducing the mass of the solids by approximately 40%. The resulting “carbonized” solids are made into a slurry ;that is thermally dried and pelletized to a solid fuel, called E-fuel, which can be combusted directly in pulverized coal boilers, gasifiers, fluidized bed incinerators, or used off-site as an alternative fuel [6]. The major advantages from gasification and pyrolysis are: (a) destroys organic compounds, (b) synthesis gas can be used as chemical feedstock or, after additional processing, as a power source, (c) provides heat that can be converted to steam and power, (d) lower volumes of flue gas and NO_x emissions than incineration, (e) low dioxins/furans and (f) produces stable solid residues that allow further recycling. The major disadvantages are: (a) some processes produce char, that requires further disposal, (b) safety issues, especially with pure oxygen, (c) complex processing, (d) no current cost data and (g) limited operating data [21].

3.5. Wet air oxidation (WAO)

Wet oxidation is a chemical oxidation of sludge (by addition of O_2) at high temperature (150–330 °C) and high pressure (6–20 MPa). ZIMPRO-process was the oldest process based on the wet oxidation technology, developed in Netherlands in 1960s. However, high energy-costs, corrosion and odor problems were the major drawbacks of the process [22]. Lately there has been new interest as addition of catalysts has made it feasible to lower pressure and temperature (Bayer Leprox-process) [23]. The main output of the process is sludge containing more than 95% of mineral components and less than 3% of low-molecular organic substances. The sludge is dewatered and then recycled or landfilled [21]. Moreover, a commercial technology named ATHOS is also based on the wet air oxidation of sludge. This consists of heating sludge in the presence of an oxidizing gas (oxygen), which will degrade organic materials. The oxidation of sludge's organic matter produces water, carbon dioxide and easily biodegradable organic compounds (acetic acid, fatty acid).

The major advantages of WAO process are: (a) improves dewaterability, (b) low energy and no fuel requirements, (c) low

air pollution concerns (no NOx, SO_2, HCl, dioxins, furans, fly ash), (d) small footprint, (e) suitable to sludges with metal content, (f) reduction of greenhouse gas (CO_2) generation, (g) residual solids are intrinsically resistant to leaching and (h) chemical oxygen demand (COD) and volatile suspended solids (VSS) reduction of 70% and 90%, respectively,and high organic nitrogen removal (70%). However, the major limitation of the process are: (a) high capital and maintenance cost, (b) does not reduce total solids significantly (7%), (c) high ammonia production may be a problem with downstream treatment and (d) high corrosion problems have caused some operations to be suspended [21].

3.6. Supercritical water oxidation (SCWO)

Supercritical water oxidation that takes place at very elevated temperatures and pressures (typically 25 MPa and 600 °C) is a good solution for sludge disintegration. Stendahl and Jafverstrom [24] reported from pilot-plant tests in Sweden with the Aqua Reci process and conclude that the SCWO process is feasible to decompose organics to more than 99.9%. In this process, carbon and hydrogen from organic and biological constituents are oxidized to CO_2 and H_2O; nitrogen, sulfur and phosphorous form N_2, SO_4^{2-} and PO_4^{3-}, respectively; organic chlorides are converted to Cl^-; and heavy metals are oxidized to the corresponding oxides. Approximately all of these reactions have shown transformations of 99.99% at 600 °C with a reaction time of 30 s or less [25]. This means that the required reactor size is relatively small. Energy recovery from this oxidation process can occur directly by heat exchange in the reactor or from the exit flow from the reactor. In comparison to sludge incineration, SCWO has the advantage that off gas treatment is very simple, so that the costs of off gas treatment can be neglected. It is also not necessary to dewater the sludge before the oxidation process. The inorganics present in the treated sludge can easily be removed from the water phase as ash [4]. While the cost of treatment is high, the value from the SCWO method in terms of sludge volume decrease together in excess of 90% recovery of energy, coagulants and phosphate represents a value, which will offset the cost of operation [21]. However, large-scale practical experience is not available yet. Use of oxygen in the process, use of high-pressure piping, the need of high-pressure reactors, and potential corrosion problems if chlorides are present in the sludge might be bottlenecks in the acceptance and further development of this technology [4].

The main advantages of this process are: (a) high reduction of volatile solids (VS) and total solids (TS) (60–80%), (b) complete oxidation of organics (COD > 99.9% reduction), (c) low emissions (NOx, SO_2 scrubber needs; no HCl, halogens, furans, dioxins, polychlorinated biphenyls (PCB)), (d) residuals resistant to leaching, (e) appropriate to metal laden sludges, (f) complete reduction in greenhouse gases, (g) suitable to hazardous waste treatment, (h) offers heat recovery and is self-sustaining and (i) less fuel necessities. However, the major limitations of SCWO process are: (a) corrosion related problems, (b) needs safety systems for handling pure O_2 or H_2O_2 as oxidants, (c) needs high-tech reaction chambers, (d) produces ammonia, which may affect the liquid treatment process, (e) elevated capital and maintenance cost, (f) needs feed waste to be pre-thickened to 5–10%, (g) feed sludge should be homogeneous and grits free and (h) selection of oxidant, reaction time, temperatures and pressures needs pilot scale study [21].

3.7. Hydrothermal treatment

Hydrothermal treatment includes the heating of sludge in the water phase at temperatures between 150 and 450 °C in the absence of oxygen or another oxidant. Sludge hydrolysis during hydrothermal treatment resulting in the production and accumulation of high concentrations of dissolved organic compounds in the liquid phase [26]. Proteins hydrolysis results in amino acids; lipids hydrolysis produces fatty acids; and hydrolysis of fiber material and hydrocarbons leads to low molecular hydrocarbon substances such as sugars. Use of oxidants in the hydrothermal treatment, which makes the process more comparable to wet oxidation, has a positive effect on the formation of VFA. Especially, these compounds are very interesting as carbon resource, not only in the production of biogas but also in the denitrification process and the biological phosphorus removal from wastewater [27]. The liquid residue of hydrothermally treated sewage sludge can be used as a marketable fertilizer, since it comprises three principal nutrients (N, P and K). Hydrothermal treatment of sewage sludge at 190 °C and 20 bar can considerably enhance the dehydration performance of the slurry like product, then the water content can be reduced to about 55% by mechanical dehydration [28].

Moreover, additional information on the above-discussed technologies are given in Table 2, which includes the cost of treatment, environmental paybacks, improvement require, stage of development and remarks on the each discussed technology.

In summary, anaerobic treatment is aimed to produce biogas from the sludge and to improve the stability of the sludge and dewatering properties. A substantial increase of biogas production can be obtained by applying a pre-treatment step, such as microwave irradiation, ultrasonication, ozonation, high-pressure homogenizer method, chemical pretreatment with acid or alkali etc. [29]. Sludge incineration methods are progressively concentrated on energy recovery in the form of electricity and/or heat (steam). The amount of energy that can be obtained strongly depends on the water content of the sludge, modification and performance of the incineration process, and the mechanical dewatering and drying process. To sidestep the high costs of a sludge incineration system and also to enhance the energy recovery efficacy, options have been investigated to incinerate dried sludge in a coal-fired power plant. Compared to incineration, pyrolysis and gasification of sewage sludge have potential advantages. The conversion of the combustible gases of both systems into electrical power can be achieved more efficiently. Besides, valuable gases can be produced as basic chemicals. Wet air oxidation process is mainly applied in practice as a sludge conditioning process aimed to improving the dewatering properties of the sludge and to reducing the final amount of sludge. Compared with wet air oxidation processes, supercritical oxidation processes are much more complex with respect to reactor design, reactor materials and reactor operation [27].

4. Energy and resources recovery

4.1. Biogas recovery by anaerobic digestion

Biogas produced during the anaerobic digestion of the sewage sludge contains 60–70% methane, 30–40% carbon dioxide, and trace amounts of nitrogen, hydrogen, hydrogen sulfide, and water vapor. A typical composition of biogas from sewage sludge AD or landfill capture and natural gas (NG) are shown in Table 3.

Methane gas generated by anaerobic digesters is the main source of energy at a municipal WWTP. In most cases, the recovered methane is used for powering gas engines, producing electrical and thermal energy for on-site use in the treatment plant. The cost of electricity for a treatment plant is about 80% of the total operational cost, and the energy recovered through methane can cover about half of this cost [31]. Methane is a major greenhouse gas and disposal of sewage sludge to landfills would result in the methane liberation into the atmosphere through natural routes. Implementation of anaerobic digestion enhances the capture of methane, which when used for electricity instead of

Table 2
Techniques for resource recovery [27].

Techniques	Cost of treatment	Environmental paybacks	Advancement require	Development stage	Remarks
Anaerobic digestion	Low/ moderate	Energy (biogas) generation	Sludge pre-hydrolysis required to enhance biogas generation	Successfully applied at full scale	Release of phosphate and ammonia during digestion process
Incineration	High	Energy generation, minimization of biosolids quantity	Mechanical dewatering, drying, use of waste heat	Full scale	Phosphate can be recovered from ash
Co-incineration in coal fired power plant	High/ moderate	Energy generation, beneficial use of inorganics	Mechanical dewatering, drying, use of waste heat	Full scale	Relative amount that can be co-incinerated is limited
Pyrolysis and gasification	High	Valuable products recovery, minimization of biosolids quantity	Mechanical dewatering, drying, use of waste heat	In development stage	Complex process, marketing of products needs attention
Wet air oxidation	Moderate	Improvement in dewatering properties of sludge	Optimization	Applied globally in practice	Process primarily focused on sludge dewatering
Supercritical water oxidation	High	Energy generation, minimization of biosolids quantity	Reactor concept, process performance	In development stage	Complex process, Corrosion and scaling problems of the reactors walls
Hydrothermal treatment	Moderate	Biogas generation, production of valuable carbon resource for denitrification, minimization of biosolids quantity	Process performance	Practical experience limited	Removal of heavy metals can be included

Table 3
Composition of biogas generated from anaerobic digesters [30,31].

Parameter	Unit	Values
Lower heating value	MJ/N m^3	23
	kWh/N m^3	6.5
	MJ/kg	20.2
Density	kg/N m^3	1.2
Methane number		>135
Methane	vol%	50–75
Higher hydrocarbons	vol%	0
Hydrogen	vol%	<1
Carbon monoxide	vol%	<0.3
Carbon dioxide	vol%	25–45
Nitrogen	vol%	<2
Oxygen	vol%	<2
Hydrogen sulphide (and variation)	mg/L	<1000 (0–10^4)
Ammonia	mg/L	<100
Total chlorine (as Cl^-)	mg/N m^3	0–5
Other details		
Energy content	6.0–6.5 kWh/m^3	
Fuel equivalent	0.6–0.65 L oil/m^3 biogas	
Explosion limits	6–12% biogas in air	
Ignition temperature	650–750 °C	
Critical pressure	75–89 bar	
Critical temperature	−82.5 °C	
Normal density	1.2 kg/m^3	

fossil fuels, decreases the generation of CO_2 associated with energy used in a wastewater-treatment plant. Therefore, anaerobic digestion of sewage sludge is an ideal source of renewable energy and should be eligible for carbon credits [30]. Several researchers reported that the 362–612 and 275–380 mL biogas/gVS can be generated using primary and activated sludge, respectively [32–34]. The Bio-terminator$^{24/85}$ is a mesophilic anaerobic digestion technology developed by Total Solids Solution from research conducted at the University of Louisiana, U.S. This process was found capable to destroying 85% of TS in 24 h at a reactor retention time of 24 h or less. A pilot scale plant of 3.785 m^3 capacity was installed at Baton Rouge, Louisiana, U.S. in 2005 and operated for 5 months [35]. The system was observed to removed 93% VS at two days hydraulic retention time (HRT). Another commercial method "Columbus Advanced Biosolids Flow-through Thermophilic Treatment (CBFT3)", is a modification of thermophilic anaerobic digestion using a plug flow reactor. This process incorporates advanced reciprocating engines to produce electricity that supplies 40–50% of the plant electricity requirements. The overall energy efficiency of the process is 68–83% [36].

Nevertheless, with the anaerobic digestion methods, almost 20–30% of the organic matter is mineralized. A substantial increase in sludge mineralization and subsequent biogas generation (Min.+10%; Max.+145% increase in biogas/methane generation) can be achieved by employing a physical, chemical, thermal, mechanical, or biological pretreatment step, such as microwave (MW) heating, ultrasonication, ozonation, enzymatic treatment, usage of liquid jets, treatment with alkali or acids, high-performance pulse technique, or wet oxidation [29]. With regard to the assessment of the feasibility of a pretreatment method, extra biogas production, total energy balance, final amount of sludge, and the costs have to be taken into account and analyzed [4]. Several pretreatment technologies such as Cambi® (thermal), BioThelys® (thermal), MicroSludge™ (physical–chemical), CROWN® (ultrasonic) and Lysatec GmbH (mechanical) have been applied successfully at full scale in several countries [37–40,46].

The Cambi process was reported to increase the net electricity production by 27% [39]. During full-scale municipal trials, Onyeche [41] reported that high-pressure homogenization of WAS prior to anaerobic digestion was found to increase gas production by 30%. Zabranska et al. [42] reported long-term monitoring results from three full-scale installations of lysate thickening centrifuges. They reported 15–26% increase in biogas yield. A pilot-scale ozonation process (0.026 kg O_3/kg VS) to pretreat the mixed primary and secondary sludge (weight by weight ratio of 1:3.5) was started in Japan by Kurita Water Industries. The process was capable to produce 36% more energy than the control anaerobic digester. The energy input (ozonation and pumping) and the energy produced were estimated at 1923 kWh and 1736 kWh/dry metric ton (MT) sludge treated, respectively [36,43]. Xie et al. [44] studied the effectiveness of an ultrasonic treatment at a full-scale sludge digester in Singapore. The anaerobic digesters (4500 m^3 volume, sludge retention time (SRT) 30 days) were fed with sonicated sludge (20 kHz; flow rate 200 m^3/day). Over the 6-month study, the experimental system consistently produced minimally 200 m^3/day more gas than the control digester (methane production increased by 45%). Hogan et al. [45] studied the feasibility of the Sonix™ technology (20 kHz) for the pretreatment of WAS prior to anaerobic digestion at demonstration and full-scale plants (Avonmouth, U.K. and Orange County, U.S.). They reported that

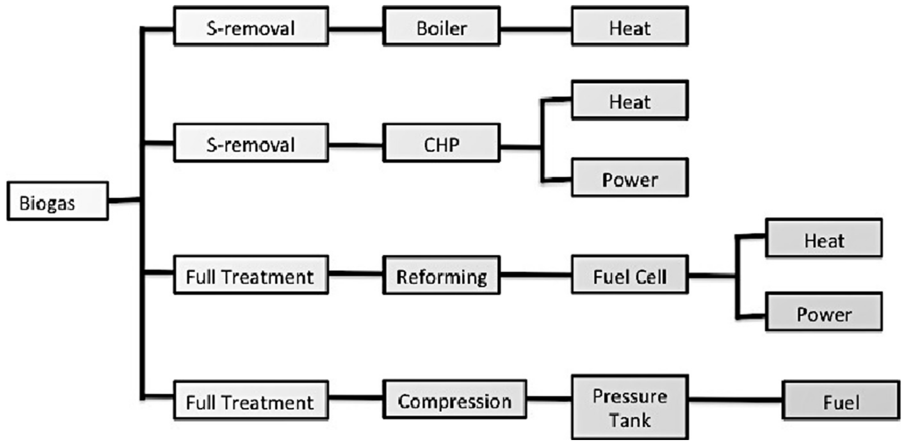

Fig. 3. Different ways of biogas utilization after proper refining and necessary treatment [30].

Sonix technology was capable to improvement in biogas production (up to 50% increase) and has a relatively short payback period of two years. The German company Hielscher (up to 48 kW) claimed to improve the biogas yield by up to 25%. Another German company Sonotronic claimed that the integration of a high-output ultrasonic reactor (20 kHz) into existing biogas production systems, increased the biogas production (up to 50%) and methane content of the biogas (up to 70% of CH_4). Barber [47] reported the outcomes of several full-scale part-stream ultrasound systems (Germany, Austria, Switzerland, Italy, Japan). He observed a 22% increase in biogas production and VS reduction, and up to 7% improvement in sludge dewatering. The energy and mass balance study of the anaerobic digester (1200 m^3, 20 days SRT, flow rate 200 m^3/day and 5% DS) treating the sludge sonicated at 2.5 W/m^2/K, shows that more energy is generated than consumed, i.e., 1 kW of applied energy will generate 7 times more electrical energy after losses. Moreover, they suggested that a typical payback period for a full-scale ultrasound installation is 2–3 years.

Biogas is an excellent fuel for large number of application and it can more or less be used in all applications that were developed for natural gas. The biogas can be used for production of heat and steam, electricity generation/co-generation, use as vehicle fuel, and production of chemicals (Fig. 3).

Biogas can be used as fuel to generate electrical power using engine generators, turbines, fuel ;cells and as fuel in gas vehicles [48]. An analysis accomplished by the combined heat and power (CHP) partnership observed that if CHP were installed at all 544 wastewater treatment facilities in the U.S. (influent flow rates $>$ 5 million gallon/day (mgd) and that operate anaerobic digesters), then approximately 340 MW (340,000 kWh) of electricity could be generated, which is enough to power 261,000 homes [6]. According to United States Environmental Protection Agency (USEPA), 2.3 million MT of carbon dioxide emissions annually (equivalent to 430,000 cars) could be offset, if existing WWTP (with capacity over 5 mgd) that employ anaerobic digestion installed energy recovery facilities. Harnessing the energy from biosolids offers energy security, a reduced dependence on fossil fuels, and lowered greenhouse gas emissions. Energy recovery from biogas is now considered as one of the more established and effective waste-to-energy conversion technologies [6].

4.2. Nutrient recovery

Sewage sludge contains considerable amounts of nutrients, especially phosphorus (0.5–0.7%TS) and nitrogen (2.4–5.0%TS) [10]; these nutrients exist mainly in the form of proteinaceous material. The breakdown and solubilization of sludge biomass and its subsequent conversion to ammonia and phosphates could potentially be used to produce plant fertilizers such as magnesium ammonium phosphate (struvite), which can be used directly for soil application [49–51]. As a rough evaluation 1 kg N and 1 kg P in commercial fertilizer costs about US$1.3 and about US$2.6, respectively. Dry solids of sewage sludge contain about 0.5 kg P and 0.6 kg N/inhabitant/year, which corresponds to a value of about US $2.1/inhabitant and year. But as long as there is no interest in this fertilizer the value is zero or agriculture has to be paid for sludge disposal [52].

Phosphorus is not a never-ending resource, because there will be no phosphorus left in apatite mines within 150 years. Thus, it should be consider as the most valuable product in the sludge. And it is necessary to develop the strategies to recover the phosphorus from the sludge, since this is one of the major available phosphorus streams presently [17]. In recent years, much effort has been directed towards phosphorus recovery from sewage sludge via crystallization, which has been developed and implemented in Japan and The Netherlands [53,54]. Calcium phosphate and magnesium ammonium phosphate (struvite) are end products that are commonly recovered from these processes. Calcium phosphate is the same chemical that is found in mined phosphate ore and is readily recycled in the phosphate industries. Struvite is an excellent plant fertilizer because of its slow release properties [50], and it can be applied directly.

In order to recover the phosphorus from sewage sludge via crystallization, it is necessary to undertake a P-solubilization process to release phosphate to the supernatant. Liao et al. [50] reported that up to 76% of total phosphorus (TP) could be released into solution using a MW heating time of 5 min. Bacterial cells and difficult-to-degrade organic compounds could be destroyed during the exposure to MW heating, which ultimately causes the release of stored polyphosphate and the phosphorus trapped in extracellular polymeric material into the solution. Ammonia is also released with the phosphate [55]. Liao et al. [56] used an advanced oxidation process (AOP) in combination with MW heating (H_2O_2+MW). They reported that more than 84% of the total phosphorous was released at 170 °C (5 min reaction time) with a 50 ml/L H_2O_2 (30 wt%) dose. Wong et al. [51] observed that the combination of H_2O_2 and acid hydrolysis resulted in up to 61% of total phosphorus and 36% of total kjeldahl nitrogen (TKN) released into the solution at 100 °C and 120 °C (5 min reaction time), respectively. Polyphosphates that formed during the MW treatment can be easily broken down by acid hydrolysis into orthophosphates [57]. Similarly, other studies also reported that a remarkable phosphorus (up to 95.5%) and ammonia (up to 53%) solubilization could be achieved by using different combination of thermo-chemical treatments [58–60]. Fischer et al. [61] presented a concept for sustainable decentralized phosphate recycling by microbial fuel cell enables phosphate recovery from digested

sewage sludge as struvite. The process yielded up to 82% or 600 mg/L. The mobilized phosphate was precipitated through the addition of Mg^{2+} and NH_4^+ as struvite, NH_4MgPO_4. The synthesized fertilizer was observed free from toxic metals such as As, Cd, Pb and Cr.

The emerging commercial techniques for phosphorus recovery from waste sludge including KREPO, Aqua-Reci, Kemicond, BioCon, SEPHOS and SUSAN are mainly based on physical–chemical and thermal treatment to dissolve phosphorus and then recover by precipitation. Phosphorus can be recovered from sludge as iron phosphate, calcium phosphate, phosphoric acid and struvite (magnesium ammonium phosphate). The Aqua Reci technology, developed in Sweden, to recover both phosphorus and energy using combined SCWO process following an extraction method [24]. About 100% of the phosphorus could be extracted with HCl or H_2SO_4 at a temperature of 90 °C and 2 h reaction time. Stendahl and Jafverstrom [24] calculated that the total cost of full scale Aqua Reci plant at Stockholm would be approximately US$946/dry MT sludge treated/year. The OSTARA process, another commercial technology to recovers struvite from a phosphorus-rich sludge stream using magnesium chloride (80–85% P recovery), has been in operation (full scale) at City of Edmonton, Canada. The process is in operation since May 2007, and is expected to produce between 200 and 250 MT of struvite/year [36,62]. A full-scale process (45,000 m^3/day) for phosphorus recovery (> 90% P recovery) as struvite (appx. 550 kg/ day; equivalent to 0.01 kg struvite/ m^3) has been installed at the Lake Shinji East Clean (LSEC) Centre in Japan [63]. The Seaborne technology, developed in Germany by Seaborne Environmental Research Laboratory [64], a two-step acid–base leaching extraction method proposed by Kungl Tekniska Hogskolan (KTH), Swedish Royal Institute of Technology [65], KREPO technique (pH 2, 100–110 °C, 3.6 bar) [66] and Kemicond™ technology (modified KREPO technique) are another efficient technologies applied at pilot and full scale for phosphorus recovery. The Crystalactor® technology was applied at full scale in the Netherlands. However, the cost of phosphorus recovery has been estimated as 22 times higher than the cost of mined phosphate rocks, and thus is not considered economical [67].

The high cost of phosphorus recovery from waste sludge (in comparison of the cost of mined phosphate rock) is considered the main hindrance in the scale up of investigated processes. Thus, out of the several methods studied for phosphorus recovery from waste sludge, most of them are either energy intensive process or studied only at laboratory or pilot scale.

4.3. Heavy metals recovery

Heavy metals such as Zn, Cu, Ni, Cd, Pb, Hg and Cr are the principal elements restricting the use of sludge for land application due to probable soil and ground water contamination, which ultimately affect the human and animal health. Therefore, appropriate treatment of the waste sludge is necessary before landfill disposal. Generally, the metal-bearing sludges are treated to extract the metal ions, or stabilize the metals in solid forms.

Thermal treatments using MW has been widely applied for the remediation of waste materials; such as pyrolysis of sewage sludges and MW assisted extraction and digestion [68,69]. Perez-Cid et al. [70] applied the four-stage Tessier sequential extraction method for metal fractionation in a sewage sludge sample. They observed the similar recoveries of Ni (98.8%), Zn (100.2%) and Cu (93.3%) using the conventional and the MW Tessier extraction methods, however, Pb extraction efficiency was excessively higher (442.5%) in MW extraction method as compare to Tessier sequential. In their successive study, almost similar findings were reported by Perez-Cid et al. [71] for Cr, Ni, Pb and Zn (recoveries between 93.9% and 102.3%). Kuo et al. [68] observed that at a solid to liquid (S/L) ratio of 0.17, 85% and 79% of Cu was leached from industrial sludge after 10 min of MW assisted treatment using nitric and sulfuric acid, respectively, however, 81% and 79% of Cu was leached after 48 h of traditional acid extraction method using nitric and sulfuric acid, respectively. Jamali et al. [72] studied the effects of the MW treatment on the extraction of Cd, Cr, Cu, Ni, Pb and Zn from the sewage sludge, and they observed overall metal recoveries of 95.3–104%. Wu et al. [73] also reported that 90% of Cu can be extracted from coarse sludge (< 9.5 mm) and fine sludge (< 150 μm) after MW-H_2SO_4 (1 N) treatment at 800 W for 20 min reaction time.

The effect of ultrasonication assisted acid leaching process on the separation and recovery of Cu and Fe from the printed circuit board (PCB) waste sludge was studied by Xie et al. [74]. The Cu and Fe leaching efficiency of 97.83% and 1.23%, respectively, was achieved at pH 3, sonication power of 160 W and leaching time of 60 min. The leaching efficiency of Cu was increased with increasing the ultrasonic power and treatment time [75]. This technique has been successfully implemented at industrial scale in a heavy metal recovery plant in Huizhou city, China from more than 2 years. The pilot-scale installation has treated 5800 t of waste sludge from PCB factories in the year 2007. From it, 1000 t 98% copper sulfate and 3500 t 20% ferric chloride were produced. All the copper sulfate was sold in market and ferric chloride was reused in local PCB manufacturing industries. No second pollution was produced by ultrasonication-assisted acid leaching method. This process shows better separation and recovery efficiency, low recovery cost, greater end product quality, and zero process waste emission [74]. In other study [76], similar group reported significantly higher recovery rates of Cu (97.42%), Ni (98.46%), Zn (98.63%), Cr (98.32%) and Fe (100%) with two-stage ultrasonically enhanced acid leaching process (4.0 pH, 100 min contact time, and 100 W power). The laboratory-verified process performance parameters (pH, ultrasonic power and contact time) were successfully applied at pilot scale treatment and almost similar recovery rates were achieved for all the studied metals as observed at laboratory scale.

4.4. Bio-fuel production

Biofuels are the solid, liquid or gaseous fuels, which are mainly produced from biomass. Biofuels gained a worldwide attention because they have the potential to replace the non-renewable petroleum fuels in future. Emerging research is focused on the biofuel recovery especially bioethanol, biodiesel, syngas and biohydrogen, bio-oil etc. from biomass [77]. Table 4 shows the major benefits of biofuels.

Biofuels are produced from sources such as corn, soybeans, flaxseed, rapeseed, sugarcane, palm oil, sugar beet, raw sewage sludge, food scraps, animal parts, and rice [79]. Using waste sludge as the substrate for biofuel production offers several advantages over the use of other biomass sources. It is a waste product and so is available at little or no cost and the supply is plentiful, since it produced wherever there is substantial human settlement [80].

4.4.1. Hydrogen

Hydrogen is a promising alternative energy to fossil fuels. It is environmental friendly in that the by-product from its combustion with oxygen is water. Hydrogen has high energy (122 kJ/g) that is 2.75 times greater than that of hydrocarbon fuel. Hydrogen can be produced from chemical and biological processes [81].

The possibility of producing hydrogen-rich fuel gas, by thermochemical treatments of wet sewage sludge that including drying, pyrolysis and gasification was studied by several researchers. Wet sewage sludge pyrolysis at high temperature (1000 °C), combined

with high heating rates enhances the production of H_2-rich fuel gas [82]. Moreover a gaseous product of much higher H_2 percentage is produced from pyrolysis of wet sludge rather than dry [83]. The extreme moisture content of sewage sludge generates at high temperatures, and a steam-rich atmosphere leading consequently to an in situ steam reforming of the volatile compounds and to a partial gasification of the solid char, which contributes to the production of hydrogen-rich fuel gas [84]. CO_2, CH_4, and H_2 concentration, low heating value (LHV) of the produced gas and aqueous yield increased by increasing moisture content, while CO concentration and tar yield decreased [83].

Biologically, hydrogen can be produced by photosynthetic and fermentative methods that are more environmental friendly and less energy intensive than chemical processes. Recently, utilization of activated sludge as the biological material for the production of hydrogen and methane using anaerobic digestion processes has received much attention [85]. However, the poor efficiency of the hydrolysis that occurs in anaerobic processes demands the pretreatment of sludge to break down the bacterial cells, reduce the SRT and increase the hydrogen yield [86]. Massanet-Nicolau et al. [80] reported that hydrogen was produced successfully (18.14 L H_2/kg DS) by fermenting (at pH 5.5) primary sewage sludge, which had been both pre-heated at 70 °C and digested with a commercially available enzyme preparation. In there following study, Massanet-Nicolau et al. [80] reported the hydrogen production of 27 L H_2/kg VS from primary sewage biosolids (pretreated at 70 °C for 1 h and with enzymatic addition i.e. 5% by volume) via mesophilic anaerobic fermentation in a continuously fed bioreactor (12 h HRT, N_2 sparging at 0.06 L/min). An 82% higher hydrogen production was observed for pretreated sludge in comparison with non-pretretaed sludge. Wang et al. [87] pretreated the WAS with UV irradiation at 25 W for 15 min and observed the cumulative hydrogen production of 138.8 mL/g TS during the batch anaerobic fermentation (mesophilic, 35 °C), which was 80.6% higher than the non-pretreated sludge (76.8 mL H_2/g TS). Guo et al. [88] investigated hydrogen production during anaerobic digestion (inoculated a new strain of *Pseudomonas* sp. GZ1: EF551040) of MW-pretreated WAS (560 W, 2 min). They observed a remarkable increase in the specific hydrogen yield to 11.04 mL/g total COD (TCOD) (18.28 mLH_2/g DS) at a lag time of 10 h. Thungklin et al. [86] observed the hydrogen production from waste sludge of a poultry slaughterhouse WWTP (5%TS) by anaerobic batch fermentation. Sludge was heated with MW irradiation at 850 W for 3 min. They registered a higher hydrogen yield (12.77 mL H_2/g TCOD) than observed for the raw sludge (0.18 mL H_2/g TCOD).

The effect of ultrasonication on hydrogen production using anaerobic digester sludge was investigated by Elbeshbishy et al. [89]. They observed a 120% increase in volumetric hydrogen production over the untreated sludge at an optimized sonication energy of 79 kJ/g TS and in temperature control conditions ($<$ 30 °C). Guo et al. [90] observed a significant increase of 1.30 and 1.48 fold in hydrogen production rate with direct ultrasonication and when ultrasonication was applied to the solution, respectively, at optimum power density of 130 W/L and sonication time of 10 s.

The effect of combined co-digestion of rice straw and sewage sludge (raw and heat-treated) on bio-hydrogen production was studied by Kim et al. [91]. Under the optimum treatment conditions (carbon to nitrogen, C/N ratio—25) high and stable hydrogen content (58%) and the maximal hydrogen yield (0.74 mmol H_2/g VS added straw) were obtained.

Reactor configurations can also affect the hydrogen yield. Gavala et al. [92] reported that the hydrogen production rate in the up-flow anaerobic sludge blanket (UASB) reactor (19.05 mmole H_2/h/L) was significantly higher than that of the continuous stirred tank reactor (8.42 mmole H_2/h/L) at low HRT of 2 h. Wu and Chang [93] used a novel composite polymeric material comprising of polymethyl methacrylate, collagen, and activated carbon entrap biomass for H_2 production with 50% yields. According to Lin and Lay [94], a C/N ratio of 47 provides the optimal H_2 production based on the microflora ability to convert sucrose into H_2 i.e. microflora H_2 production rate. The specific H_2 production rate increased with increasing temperature from 33 to 39 °C, then decreased as the temperature was further increased to 41 °C [95].

Table 4
Major advantages of biofuels[78].

Economic impacts	Sustainability
	Fuel diversity
	International competitiveness
	Reducing the dependency on imported petroleum
Environmental impacts	Greenhouse gas reductions
	Reducing of air pollution Biodegradability
	Higher combustion efficiency
	Carbon sequestration
Energy security	Supply reliability
	Reducing use of fossil fuels
	Ready availability
	Renewability

4.4.2. Syngas (H_2+CO)

Syngas, a mixture of carbon monoxide and hydrogen, could be used as a clean alternative to fossil fuels in electricity generation or for the production of liquid fuels such as synthetic diesel, dimethyl ether and methanol [96]. The syngas production is a two-step process. In the first step, the pyrolysis of sewage sludge at around 600 °C in an oxygen-deficient atmosphere takes place, which leading to the production of carbon rich char. In the second step, the char is gasified in the presence of oxygen or air and produces the syngas. Lv et al. [96] investigated the pyrolysis of sewage sludge at 1040 °C and they reported that both H_2 and syngas were produced in a higher proportion with maximum values of 38% for H_2 and 66% for syngas. Zuo et al. [97] used activated carbon as MW receptor to enhance the syngas production. They observed that the presence of activated carbon enhanced the concentration of syngas (60%) in the pyrolysis gas, which having a high calorific value of 12.930 MJ/nm^3. A commercial method, EBARA fluidized bed gasification technology (Japan), co-treats municipal sludge with other solid wastes, including municipal solid waste, plastic waste, medical waste and fly ash to recover the energy rich syngas. As of September 2002, six TwinRec process lines were in operation and 14 more were under construction [98].

4.4.3. Bio-oil

Bio-oils, components of *n*-alkanes and 1-alkenes, aromatic compounds (that range from benzene derivatives to PAH, nitrogenated compounds, long-chain aliphatic carboxylic acids, ketones, esters, monoterpenes and steroids), which are refined to high-quality hydrocarbon fuels, might have some advantages including facility of transport, storage and combustion and flexibility in marketing [99]. Furthermore, the bio-oil is a possible source of light aromatics for example benzene, toluene, and xylene, which control a greater marketplace value than raw oils [100].

Sludge pyrolysis (liquefaction) at intermediate temperatures of around 425–575 °C (heating rate around 100 °C/min) allows the dominant production of bio-oil, the yield of which amounts to 30–40 wt% of sewage sludge [5]. There have been studies where the sludge has been converted thermally to liquid and solid fuels; oil yields have ranged from a low of 13% for an anaerobically digested sludge to a high of 46% for a mixed raw sludge [101]. Table 5 summarizes the outcome of various studies carried out to convert the waste sludge in energy rich bio-oils.

Table 5
Bio-oil recovery from waste sludge.

Type of sludge	Treatment conditions	Bio-oil yield (%)	Calorific value (MJ/kg)	Source
Primary sludge (84% VS)	Electric, batch, 500 °C, 20 min	42	37	
Waste activated sludge (69% VS)	Electric, Batch, 500 °C, 20 min	31	37	[214]
Anaerobically-digested sludge (59% VS)	Electric, Batch, 500 °C, 20 min	26	37	
Anaerobically digested sludge (38.3% VS)	Electric, continuous, 550 °C	24.3	30.6	[12]
Sewage sludge (75.5% VS)	Electric, batch, 500 °C, 30 min	37	30	[100]

In 1980, a pilot scale study was carried out to produce the bio-oil from waste sludges using thermo-chemical liquefaction, where liquid sludge (20%TS) was heated at 300 °C and 10 MPa pressure for about 90 min, generating a heavy oil, char, gas and reaction water. The technology was patented as Sludge-to-Oil Reaction System (STORS). Typically oil yields ranged from 10% to 20% and char from 5% to 30% by weight. Conventionally, liquefaction of sludge is always carried out in an electric or gas furnace [99]. Unfortunately, many of the oils that are obtained at high pyrolysis temperatures (above 700 °C) contain high concentrations of PAH, which are known to have carcinogenic or mutagenic characteristics [102] and lead to environmental pollution on combustion. Therefore, MW-induced pyrolysis, which allows the use of high temperatures with the minimum production of PAH, was considered a possible alternative for bio-oil recovery from waste sludge. The pyrolysis oils produced have a high calorific value and a low proportion of compounds of environmental concern (such as PAH) [99]. Tian et al. [100] observed that for short residence times and high heating rates, MW pyrolysis resulted in a maximum oil yield of 49.8 wt% in 6 min with negligible PAHs and with favorable characteristics such as a high calorific value (35.0 MJ/kg), low density (929 kg/m^3) and preferable chemical composition (29.5 wt % monoaromatics). Furthermore, sulfur and nitrogen were mainly restrained to solids.

Bio-methanol is also considered to play a significant role as a synthetic fuel in the future. The important advantages of methanol as a fuel are a higher energy content per volume than compressed natural gas or liquefied petroleum gas, and minimal changes in the existing fuel distribution network. Finally, methanol can considerably reduce automotive emissions and requires no antiknock alternatives, because of its high octane number. Sewage sludge contains a reasonably high fraction of organic material, which is rich in carbon—the main constituent of methanol. The second constituent of methanol, hydrogen, can be obtained from water present in wet sludge during the gasification process. Ptasinski et al. [103] investigated the sludge gasification method to produce the methanol. They observed that overall conversion degree of carbon present in the sludge into methanol equal to 57%. The methanol—from—sludge process depends on the dry solids content of the sludge leaving the thermal dryer, and on the gasifier temperature. From the point of view of the overall rational efficiency the optimal conditions are a dry solids content of 80 wt% and a gasifier temperature of 1000 °C.

The commercial EnerSludge™ demonstration plant was installed at Perth, Australia. Overall 45% energy in the biosolids was converted to bio-oil, however, the plant was discontinued after 16 months of operational period because it was not considered cost-effective [104]. In another STORS process, which was commercialized by ThermoEnergy [105], at high pressure and elevated temperature (275–315 °C, 11,400–14800 kPa and 1–3 h), the sludge (20% DS) was converted into a fuel consisting of oil with 90% of the heating value of diesel, and a solid (char) similar to coal. The recovered bio-oil can be used to generate electricity and/or heat using an engine. A general cost estimate of STORS technology for small (10,000 p.e., 292 dry MT/year), medium (100,000 p.e., 2920 dry MT/year) and large size (1 million p.e., 29,200 dry MT/year) population was provided by Molton et al. [106]. They estimated the energy used in the process were 1410, 1394 and 1394 kWh/dry MT, and the electricity from oil produced were 1898, 1480 and 1480 kWh/dry MT for the small, medium and large size population, respectively. However, there is currently no full-scale installation in operation [36].

4.4.4. Bio-diesel

Limited fossil fuel reserves and environmental benefits of biodiesel (decrease in acid rain and emission of CO_2, SO_x and un-burnt hydrocarbons during the combustion process; easy biodegradability; less toxic; safer for storage and handling) increase the significance of biodiesel [107]. Biodiesel is the esters of simple alkyl fatty acids that can be produced from various lipid sources by trans-esterification reaction with alcohol in the presence of a base, acid, enzyme or solid catalyst. Municipal sewage sludge is gaining traction in the worldwide as a lipid feedstock for biodiesel production. Because, it is available in abundance and contains significant amounts of lipids, which can make biodiesel production from sludge lucrative. These energy-rich lipids include phospholipids, monoglycerides, diglycerides, triglycerides and free fatty acids comprised in the oils and fats [108]. Fig. 4 shows the overall biodiesel production scheme.

In order to enhance the biodiesel production, it is recommended that wastewater operators employ the microbes that are selected for their oil-producing capabilities. This could enhance the biodiesel production to the 10 billion gallon mark, which is more than three times the current biodiesel production capacity of US [108]. Moreover, the studies [110] shows that combining lipid extraction processes in 50% of all existing municipal WWTP in the US and trans-esterification of the extracted lipids could produce approximately 1.8 billion gallons of biodiesel, which is about 0.5% of the yearly national petroleum diesel demand. Currently, the estimated cost of production is US$3.11/gallon of biodiesel. Nevertheless, this cost should be reduced to levels that are at or below the current petro diesel costs of US$3.00/gallon [108]. According to Kargbo [108] and Siddiquee and Rohani [109], biodiesel production from waste sludge is facing the following upcoming challenges;

(i) *Sludge pre-treatment*: The pre-treatment of raw sludge i.e. collecting, dewatering and drying can significantly affect the lipid extraction process and consequently the yield and cost of biodiesel production. The lipid extraction from dried sludge is feasible and vacuum drying can be a good option.
(ii) *Efficient lipid extraction*: Solvent selection, sludge to solvent ratio, extraction time, temperature and solvent recovery are among the factors that affect the lipid extraction efficacy and cost. Optimization of these factors is necessary for efficient lipid extraction.
(iii) *Efficient production of biodiesel*: The optimum production of bio-diesel is fronting the big challenges. First, extraction and then trans-esterification of lipids containing fatty acids. Second, reaction completeness (> 98% complete) and fuel deterioration (acid value) continue to be challenging aspects of bio-diesel production. Third, the careful selection of catalysts

is a key component of successful biodiesel production from lipid feed stocks such as sludge.

(iv) *Maintaining product quality*: There is a prerequisite to carefully select and assess the effectiveness of the trans-esterification process to treat pharmaceutical chemicals (emerging contaminants) and a high concentration of free fatty acids (FFA) (which can result in problems such as soap formation and difficulty in product separation) present in sludge and to produce best quality biodiesel.

(v) *Economical aspects of biodiesel production*: The cost of production has hampered its growth and made it uncompetitive in comparison of petro diesel. The cost of raw materials (feedstock) accounts for 80% of the total biodiesel production cost [111], which makes the availability of cheap and reliable biodiesel feedstock a very important issue in biodiesel production. The biodiesel production using sludge as feedstock can reduce the cost considerably. Lipid extraction and biodiesel production from sewage sludge is associated with the use of organic solvents and more than 99% of the solvents are recoverable [112].

Currently, the estimated cost of production of biodiesel from dry sludge is US$3.11/gallon of biodiesel [113,114] compared to US $3.00/gallon for petro diesel (as of January 2010).

To be more reasonable, it is necessary to reduce the cost up to the levels that is equal or under petroleum diesel costs. Mahamuni and Adewuyi [115] reported that the use of high-frequency ultrasound significantly reduces the costs of biodiesel production. Angerbauer et al. [116] observed that the pretreatment of sludge by ultrasonication, can make lipids accessible to *L. starkeyi* (a yeast) and they accumulated a high amount of lipids i.e. approximately 70% of dry matter. Moreover, the best results were obtained with ultrasonication pretreatment in comparison of alkaline/acid hydrolysis or thermal treatment. According to Spinosa [17], recovery of readily utilizable and storable liquid fuels, provision of net energy yields, generation of greenhouse credits, complete control of heavy metals, destruction of organo-chlorine compounds, complete destruction of pathogens, odor control, small footprint for plant, minimization of material requiring trucking off-site are the major advantages, however, the main disadvantage is the capital-intensiveness and the relative complexity of the plant. Thus extensive efforts are required to optimize the methods for efficient and economic biodiesel production from waste sludge.

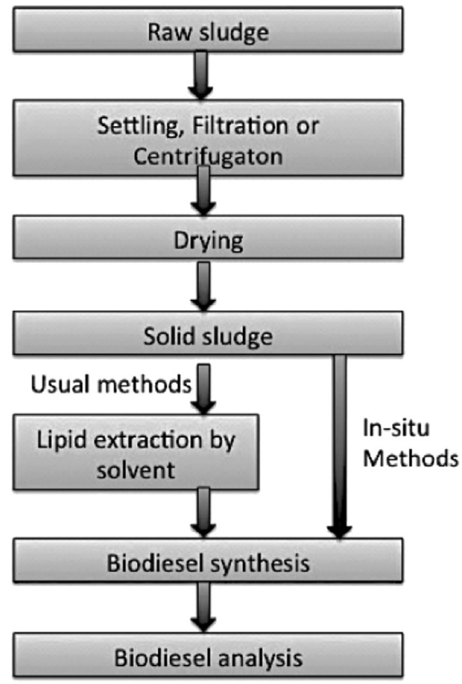

Fig. 4. Schematic of biodiesel production from waste sludge [109].

4.5. Construction material

Reuse of waste sludge for construction materials can reduce the problems of disposal, while offering a renewable substitute for depleting non-renewable resources. This approach will provide a great potential for massive waste utilization [117]. Sewage sludge containing both the organic carbon-containing complexes and the inorganic composites, represent to a source of valuable materials. A substantial work has been carried out for manufacturing of valuable products by thermal solidification of the inorganic sludge composites, particularly in Japan. Dried sludge or the incinerator ash is used as a primary material in manufacturing of construction material. The solidification process occurs at high temperatures i.e. up to 1000 °C. Waste heat is available for the drying process. Dependent upon the specific process modifications and the applied operating conditions, various types of products can be made, such as artificial lightweight aggregates, slags, and bricks [8,118].

Upon mixing with clay or on their own, biosolids ash can be used to make bricks that are similar in appearance and physical properties to standard building bricks [119,120]. In Japan, biosolids ash has been used to make bricks for over a decade [121]. First full-scale sludge brick plant was commenced in 1991 in Tokyo with a production capacity of 5500 bricks per day using 15,000 kg of incinerated sludge ash. More importantly, no heavy metals leaching was observed from the finished bricks, even in adverse environments with pH levels as low as 3 [17]. Anderson et al. [122] added sewage sludge ash from a fluidized bed incinerator to a series of common commercial brick; they reported encouraging results that directed a United Kingdom brick company to use this material as a potential substitute for the sand addition to the bricks. At the University of Leeds, U.K., Forth [123] has recently produced a building block “Bitublock”, made by mixing waste products like recycled glass, sewage sludge, metal slag and incinerator ash with a sticky binder called bitumen. Bitublock was considered almost six times stronger than traditional concrete block. Waste sludge can also be used to produce the pumice, which consists of highly vesicular rough textured (characterized by a rock being pitted with many cavities, known as vesicles, at its surface and inside). It can be used for the under-layer of athletic grounds as it has the characteristics to drain the excess water and hold sufficient moisture. Generally, volcanic gravels are used for this purpose, thus pumice can be good alternate of scarcely available volcanic gravels [17].

The production of Portland cement using the waste sludge is another way to use valuable inorganic and organic compounds of the sludge [124]. The waste sludge can be used in three different forms as incinerated ash, dewatered sludge, or dried sludge powder. Out of three forms, use of dewatered sludge directly into Portland cement kilns seems to be the highly appealing. As this process is neither requiring new incinerators nor generating additional running cost. At high operating temperature, toxic organic pollutants in the sludge are completely oxidized, and heavy metals are immobilized in the cement [4]. Thus sludge can be a used as a raw material in Portland cement manufacturing, and subsequently reduce the burden from natural resources like clay and limestone (source of CaO, SiO_2, and F_2O_3) [17]. According to previous studies [125–127], cement-like materials made from sludge can replace ordinary Portland cement for up to 20% by weight.

Waste sludge can also be reused in manufacturing of artificial lightweight aggregate (ALWA). ALWA can be used as planter soils, fillers for clearance between kerosene storage tanks and room

walls, flower pot additive, heat-proofing panel, water-infiltrating pavement replacement of anthracite media in rapid sand filters as well as in walkways paved with ALWA [17]. A 500 kg/h plant for producing ALWA commenced operations in 1996 at the Nambu plant in Tokyo. Compared with commercial lightweight aggregates, ALWA has better sphericity, lesser specific gravity, and low compressive strength. Concrete made with the sludge–clay aggregates had a lower density and hence a higher strength to mass ratio as compared with that produced from conventional granite aggregates. On the basis of their research findings, Tay et al. [117] recommended that the sludge–clay aggregates with up to 20% clay content are suitable for structural applications, while the aggregates with up to 50% clay content could be used for other general applications where strength is not a critical requirement. The leaching test results showed that the peak levels of all health-based contaminants were within the respective safety limits specified in the World Health Organization (WHO) guidelines for drinking water. The compliance to WHO safety limits indicates that the use of these sludge–clay aggregates should not have significant effect on human health or the environment.

Slag, a marble like mineral of semi-crystalline structure, is a possible solution of volume reduction and the immobilization of heavy metals in sludge. Water-cooled slag and air-cooled slag are two types, which can be produced from waste sludge, and can be used as an alternative for natural coarse aggregate, including ready mixed concrete aggregate, roadbed materials, concrete aggregate and back-filling material, interlocking tiles, permeable pavement, and other secondary concrete products [17]. GlassPack®, a vitrification process (developed by Minergy Corporation, U.S.), uses the organic fraction of biosolids as a renewable fuel source to produce an inert glass aggregate product from the inorganic (ash) fraction. Wet sludge (approx. 20% solids) is pre-dried to $<15\%$ moisture; the dried solids are then subjected to temperatures between 1330 °C and 1500 °C, at which the ash component melts into molten glass.

Thus the promising output was reported worldwide regarding the use of waste sludge as construction material. Nevertheless, despite the development of technically feasible processes, most of the techniques are not economically viable due to the higher production cost (if compared to market price). Therefore, the commercialization of sewage sludge based construction material i.e. scale up of economical feasible technologies and market development are the major challenges.

4.6. Electricity production from sludge by microbial fuel cells

Electricity production from sludge using microbial fuel cells (MFC) has been considered as a beneficial way for sludge reuse. A mixed bacterial population can be used in MFC to produce the electricity while achieving the biodegradation of organic wastes. Many different bacterial species including *Escherichia*, *Shewanella*, *Clostridum*, and *Desulfovibrio* have been reported to reduce metallic ions (e.g. manganese, ferric, uranium, and cupric), while oxidizing the available carbon substrates by redox mechanism [128–131]. Rabaey and Verstraete [132] describe the mechanisms of waste treatment in MFC reactors. Microbes in the anodic chamber of an MFC oxidize added substrates and produce electrons and protons in the process. Electric current generation is made possible by keeping microbes separated from oxygen or any other end terminal acceptor other than the anode and this requires an anaerobic anodic chamber. Typical electrode reactions are shown below using acetate as an example substrate.

$$\text{Anoidic reaction}:\ CH_3COO^- + 2H_2O \xrightarrow{\text{microbes}} 2CO_2 + 7H^+ + 8e^- \quad (2)$$

$$\text{Cathode reaction}:\ O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad (3)$$

The whole reaction is the decomposition of the organic substrate to carbon dioxide and water with a simultaneous electricity generation as a by-product. Based on the electrode reaction pair above, an MFC bioreactor can generate electricity from the electron flow from the anode to cathode in the external circuit [128].

The voltage of a biofuel cell is normally in the order of several hundred millivolts (mV). Power densities in the order of 50–100 W/m^3 reactor have been reported [133]. The performance of a MFC depends upon many process and system parameters, such as pH, temperature, type of substrate, amount of soluble substrate in sludge, type of bacteria, type of electrodes, internal resistance, etc. [134,135]. The possibility for the application of a MFC in sludge treatment has been investigated by Dentel et al. [136]. They observed that an electrical current of about 60 μA maximum could be obtained and a potential of several hundreds of mV. Jiang et al. [135] used a two-chambered MFC to generate electricity from ultrasonically pretreated sewage sludge. They reported that stable electrical power was produced continuously during operation for 250 h, together with 46.4% TCOD reduction. Moreover, the MFC produced power was observed in close correlation with the SCOD of sludge.

The wide scale acceptability of MFC process will depends upon not only the microbial electricity production process itself, but also the effect of this process on the residual sludge amount and sludge composition [4]. The present scientific efforts are toward the development of the large-scale microbial fuel cells for the conversion of waste sludge and other organic waste to electricity. However, substantial research is required to scale up this technique in terms of efficient and economic operation.

4.7. Bio-plastic

Polyhydroxyalkanoates (PHA) are polyesters of hydroxyalkanoic acids and are well-known as biodegradable thus environment friendly alternative to petroleum plastics [137–139]. Poly-β-hydroxybutyric acid (PHB) and its copolymer poly (3-hydroxybutyrate-co-hydroxyvalerate [P(3HB-co-HV)]) are the most widespread PHAs, while other forms are possible [140]. PHA produced in nature by bacterial fermentation of sugar or lipids. PHA in microorganisms, particularly in bacteria, serves as carbon and energy reserve and/or as sink for redundant reducing power or electrons in stressful states [141,142]. Several microorganisms can accumulate PHA; however, its widespread applications have been restricted due to high production costs. Considerable efforts have been made to improve the yield of PHA by microbial fermentation and diminish the production cost. The new method involves the use of renewable carbon resources derived from agriculture or industrial waste and/or waste activated sludge as a substrate or source for PHB accumulation [143–145]. These methods have the advantages of reducing cost of PHA production and volume reduction of waste sludge by extracting PHA [144]. PHA accumulating microorganisms are found in activated sludge. The polyphosphate accumulating organisms (PAO) accumulate PHA by taking up VFA under anaerobic conditions. PHA production by activated sludge has the following advantages [146]: (1) by using activated sludge, waste organic materials can be recovered and reused as biodegradable plastics, (2) the cost of PHA production can be reduced by using waste sludge as feedstock because the waste sludge is easily available in plenty and (3) PHA that are not produced by known pure cultures could be obtained by using activated sludge instead of pure cultures [147].

Microorganisms in activated sludges are capable to accumulate PHAs ranging from 0.30 to 22.70 mg polymer/g sludge [148]. Yan et al. [149] used the pulp and paper mill WAS as a source of microorganisms to produce biodegradable plastics (PHA) at 25 °C, pH 7 and acetate as the sole carbon source. Maximum accumulation

of PHA (39.6% w/w of dry sludge SS) was observed at 15 g/L SS and 10 g/L acetate concentration [149]. PHA recovery using activated sludge is controlled by several operating parameters. Although activated sludge acclimatized under anaerobic–aerobic conditions accumulates PHA, however, earlier studies showed that PHA accumulation can be enhanced by introducing a small quantity of oxygen into anaerobic zone [150,151]. Takabatake et al. [152] reported that PHA accumulation capability of sludge was 20–30% for fully aerobic sludge, 17–57% for anaerobic–aerobic sludge, and 33–50% for microaerobic–aerobic sludge. Takabatake et al. [153] also observed that average PHA content after the aerobic incubation was 18.6%, with the minimum of 6.2% to the maximum of as high as 29.5%. They reported that activated sludge in conventional process had a higher PHA accumulation capability than that in anaerobic–aerobic process. Temperature is another parameter, which control the PHA production and storage by activated sludge. The findings of Krishna and van Loosdrecht [154] revealed that PHA production increased with a decrease in temperature. Moreover, operating pH≥8, lower solids concentration in reactor and shorter SRT favorably affect the PHA production rate [143]. Process configuration was also considered to play an important role in PHA production. Sequencing batch reactors (SBRs) were suggested as ideal reactors for higher PHA production, due to highly flexible operation, easiness in control and biomass growth under transient (unsteady) conditions [101].

PHAs are appealing as packaging films and disposable products (i.e. utensils, diapers, cosmetic containers, bottles, cups, etc.) due to their biodegradability [155]. In medicine, PHA can be used as functionalized nano/micro-beads for diagnostic and therapeutic applications, for soft and hard-tissue repair and regeneration, as conduits and carrier scaffolds for nerve repairs, as drug delivery systems, as devices for joints and wound dressings, as drug eluting stents for cardiovascular applications, and as heart valve in heart tissue engineering [156–161]. Several PHA products such as Biopol, Mirel and Nodax (USA), Biomer (Germany), Biocyle (Brazil), DegraPol (Italy) and Tianan PHBV and PHB (China) are available commercially in the market [142,162]. Companies that manufacture microbial PHA include ZENECA Bio-products (UK), Biotechnolgische Froschungs gessellschaft mbH (Austria), Petrochemia Danubai, Bio Ventures Alberta Inc. (Canada), Biocorp (USA), Metabolix (USA), Procter and Gamble (USA) and Asahi Chemicals and Institute of Physical and Chemical Research (Japan) [155,158].

The current production cost of microbial PHAs is about US$4–6/kg, which is almost 10 times higher than petroleum plastic [137,140]. The cost of carbon source has triggered the slow growth experienced by the PHA industry. For example, the cost of substrate or carbon source accounts for about 50% of the microbial PHA cost [163]. Even with genetically engineered *E. coli*, the carbon source is still about 31% of PHA' production cost [164]. According to Brar et al. [165], the major technical difficulty with bioplastic production from wastewater sludge is the optimization of organic loading rate (OLR) and also economically lower yields. This requires extensive studies on enhancement of OLR and efficacy of utilizing mixed substrates (sewage sludge and agroindustry wastewater sludge) with mixed cultures.

4.8. Biosorbent

The use of biosorbent to remove heavy metals from wastewater has emerged as an eco-friendly, effective and low cost method. Waste activated sludge is considered as a good biosorbent for the removal of heavy metal ions from industrial wastewaters. Sewage sludge can be converted into activated carbon using pyrolysis process under controlled conditions or with some chemical treatment. This conversion could provide the collective paybacks of lessening the quantity of sludge and generating a valuable adsorbent of low cost than commercial activated carbon [101,166,167]. Rozada et al. [168] studied the effect of sludge-based biosorbent on the removal of dyes from colored wastewater in batch and fixed film systems. They reported that activated carbons produced from waste sludge showed a good development of their mesopore structure and excellent removal of dyes and metals. Annadurai et al. [169] used MW treated sludge for adsorption of dyes and they reported the encouraging outcomes together with energy efficiency of MW process than the conventional heating method. In another study carried out by Hsieh et al. [170], the energy cost analysis exhibited the feasibility of applying the MW process for production of sludge-derived adsorbents.

Conventionally, adsorbent materials from sewage sludge were produced by chemical activation by H_2SO_4 impregnation followed by pyrolysis. The waste sludge were initially oven dried at 105 °C and later chemically activated by soaking with H_2SO_4. The resulting sludges were then pyrolysed under inert nitrogen, and subsequently washed with dilute HCl (10% by mass). These adsorbent particles were pulverized to preferred particle sizes of greater porosity and higher surface areas [171,172]. Chen et al. [173,174] proposed an alternate method of activated carbon preparation by activating anaerobically digested sewage sludge with 5 M $ZnCl_2$ and followed by pyrolysis at 500 °C for 2 h under the N_2 atmosphere. They concluded that the proposed method could be turned out to be a cost effective option in comparison with the existing conventional methods.

Composite adsorbents, prepared by mixing sludge with a phenolic resin shows a significant removal efficiency of 98% for total organic carbon (TOC) and 32% for NH_4^+ salts, which was similar to those achieved with commercial activated carbon [175]. Many sludge-derived biosorbents suffer from the problems of leaching of organic matter and metals. However, this problem was eliminated by using the sodium and calcium alginate immobilized sludge [173]. Moreover, it was reported that sludge derived activated carbon performed better when removing dyes with a higher presence of anionic solubilizing groups and heavy metals [176,177]. The adsorption capacity of biosorbents depends on several factors i.e. pyrolysis temperature, time, and the specific chemistry of the sludge precursors [178]. Wastewater sludges have also been used as a carbon source for odorous gas treatment via adsorption and for flue gas treatment via desulfurization, although both with limited application [179].

The substantial work has been carried out on the sludge-derived biosorbents, however, most of the studies are carried out at laboratory scale. Thus pilot or full-scale studies are necessary to scale up this application with main emphasis to understand the synergistic/antagonistic effect of each pollutant with the adsorbent and its potential effects on the environment.

4.9. Bio-pesticides

Waste sludge seems to be a valuable source of carbon and nutrients like nitrogen and phosphorus for several biological methods that could add value to sludge by generating some beneficial metabolic products, such as endotoxins, spores and some other compounds (vegetative insecticidal proteins—vips, hemolysins, enterotoxins, chitinases, proteases, phospholypases and others), which are insecticidal in nature and defined with the term of entomotoixicity (or bio-pesticidal potential). To date, *Bacillus thuringiensis* (Bt) is very effective bio-pesticide being used extensively in agronomy, forestry and public health sector. Application of sewage sludge for Bt production followed by its utilization in agricultural crops and forests for pest control appear to be totally compatible with existing sludge disposal exercises [101]. The bio-pesticide production method comprises the following stages: (a) sludge fermentation, (b) product recovery/harvesting, and (c) product formulation. Barnabe et al. [180] investigated the

effect of pre-treatment schemes (alkaline and thermo-alkaline pretreatment alone and in combination with partial oxidation using H_2O_2) to improve the entomotoxicity production by Bt in secondary and mixed sludge. They observed a significant improvement in the entomotoxicity by 50% for mixed and/or secondary sludges. Several factors including pH, dissolved oxygen (DO), foaming, solids concentration and inoculum, sludge type can affects the process of bio-pesticide production [101,181–183]. Lacchab et al. [184] investigated the effects of inoculum and solids on Bt fermentation of wastewater sludge. The optimum total solids concentration was 25 g/L, which resulted in an improved entomotoxicity. Tyagi et al. [101] determined that the *Bacillus thuringiensis* Institut national de la recherche scientifique (BtINRS) process (based on wastewater and/or wastewater sludge) has been investigated at different stages of Bt production (e.g., fermentation, downstream processing and formulation (liquid suspension) development) and has shown promising results, which can be carried forward for its application in the field.

4.10. Other resources

4.10.1. Protein

Sewage sludge can be used as the protein source, because its main constituents are protein and carbohydrate. Chen et al. [185] report that the sewage sludge consists of 61% protein, 11% carbohydrate, less than 1% lipid, and over 27% unknown components on the basis of its TCOD. Protein has been estimated to account for about 50% of the dry weight of bacterial cells [186]. On the other hand, protein is one of the most important constituents in animal feed, furnishing energy and nitrogen [187]. Hwang et al. [188] applied the hybrid ultrasonic-alkaline pretreatment followed by precipitation and drying to release and subsequently recover the intracellular protein from WAS. The supernatant protein concentration was observed to be 3177.5 mg/L after pretreatment of WAS (5330 mg/L SS) with combined ultrasonication (1.65×10^{10} kJ/kg VSS)-alkaline (pH 12, 2 h) method. The maximum protein recovery of 80.5% was achieved at an optimum pH 3.3. They reported that the nutrient composition of recovered protein was comparable with the commercially available protein feeds. Chishti et al. [189] studied the effect of NaOH and NaCl alone as well as in combination for protein extraction from sludge. Of all the precipitants used, ammonium sulfate (40%) was observed most effective, providing a maximum protein recovery of 91%. Moreover, protein recovery unit processes removed most of the metals with proteins initially present in the primary sludge; the recovered product comprised all the necessary amino acids, which could serve as an animal feed supplement. The effective detoxification of sludge i.e. sterilization, removal of heavy metals and other toxicants are the necessity before effective utilization of sludge for production of animal feeds [190]. Nevertheless, utilization of sludge for production of animal feed is not a popular route till yet, which may be due to the availability of other low cost routes of nutrients like agro-industry residues, that can serve as better nutrient supplements without any compromise with animal health in terms of pathogenic and metals toxicity [191].

4.10.2. Enzymes

The extraction of enzymes is significant mainly because of: the recovery of a valuable product from the activated sludge, and second that these enzymes could be used to advance the biodigestibility of sludge and subsequent biogas generation during anaerobic digestion [192]. Based on the literature review, it is apparent that sludge can produce different enzymes e.g. Protease, glycosidase, dehydrogenase, catalase, peroxidase, α-amylase, α-glucosidase [101]. Nabarlatz et al. [192] used the ultrasonication assisted extraction method to recover the hydrolytic enzymes (protease and lipase) from the WAS. They suggested that the power intensity of 3.9 W/cm^2 and sonication time of 10–20 min were suitable to achieve a higher rate of enzymes recovery. The enzymes released by the microorganisms in activated sludge are responsible for the organic matter degradation.

Enzymes are recognized to accomplish a multitude of chemical reactions and are commercially used in the detergent, food, pharmaceutical, diagnostics, and fine chemical industries. Considering their commercial significance, cost-effective production of these enzymes is necessary. Actually 30–40% of the production cost for industrial enzymes is accounted for by the cost of the culture medium. Thus, if sludge could substitute the commercial medium ingredients, the cost benefits could be significantly high, since the sludge has zero or marginal (i.e. transportation) cost. Therefore, these sludge derived enzymes could be harvested for further reuse and other environmental applications [101]. In order to scale up the enzymes recovery from WAS, further studies must be carried out to optimize the enzyme extraction process together with and techno-economical evaluation of the processes.

4.10.3. Bio-fertilizers

The amino acid chelated trace elements (AACTE) fertilizer is recognized as an environmentally friendly fertilizer for cotton, fruits and other cash crops in China [193]; however, its production is restricted by limited protein sources such as animal hair, hoof, horn, and leather [194]. Liu et al. [195] developed a novel technology for sewage sludge utilization. The bacteria proteins in the sewage sludge were extracted to generate the AACTE fertilizer using several chemical methods. Initially, the sewage sludge was hydrolyzed under hot HCl solution to obtain protein solution. Then, protein solution was further hydrolyzed into amino acids in hot acidic condition. After that, raw amino acids solution was purified through activated carbon decolorization and glacial acetic acid dissolution. Lastly, the purified amino acids were used to produce the AACTE fertilizer by chelating with trace elements. The optimum hydrolysis condition for the protein extraction from the sewage sludge was pH 0.5, hydrolysis temperature = 121 °C and reaction time = 5 h, while that for protein hydrolysis into amino acids was hydrolysis temperature = 120 °C, reaction time = 10 h and the ratio of 6 mol/L HCl solution (mL) to dry sludge (g) = 8. Under optimum hydrolysis conditions, 78.5% of protein was extracted from the sewage sludge and the amino acids yield was 10–13 g/100 g of dry sludge. The AACTE fertilizer produced was observed in agreement of China Standard for Amino Acids Foliar Fertilizer (GB/T 17419-1998) [194].

4.10.4. Volatile acids

Several volatile acids such as acetic acid, formic acid and propionic acids can be recovered from waste sludge using anaerobic bio-digestion, or thermal processes such as wet air oxidation [196]. Shanableh and Jomaa [26] reported that an optimum amount of VFA could be produced at moderate hydrothermal treatment (<200 °C) of waste sludge. The recovered volatile acids can be serve as a chemical feedstock, nevertheless, no developments in this area were identified [36].

5. Global scenario of beneficial reuse and resource recovery from waste sludge

Since past few years, there is a general consensus among the wastewater treatment experts worldwide that waste sludge is not a waste, but a source of valuable resources. The major factors behind this consent are sustainability and environmental concerns (resource depletion, soil pollution and global warming); hike in energy prices, stringent directives for sludge disposal and increasing pressure and protest from environmental authorities and from the public domain

[36]. Japan may be considered as one of pioneer country in production of construction materials from sewage sludge. Sludge is used to produce the construction materials at full-scale plants [197]. The Sewerage Bureau of Tokyo Metropolitan Government (SBTMG) implemented several projects including the use of dewatered sewage sludge to produce fuel charcoal and sold for thermal power generation [198] and, for the electricity generation with a gas engine using syngas produced by pyrolysis of sewage sludge [199]. Since 1990, the Swedish government has emphasized the significance of nutrient recycling from sewage sludge. Thus use of sludge in agronomy is not a common practice, despite the low concentration of contaminants in sludge compared to other countries [200]. In 2000, the Swedish government investigation projected the target of recycling 75% of the phosphorus from waste and sludge to productive soils by 2010 [201]. In several Swedish cities, use of sludge derived biogas as biofuel in transportation sector is a well-established practice. The Herenriksdales treatment plant produces and sells biogas to Stockholm's bus company. At least 30 buses in Stockholm are running on biogas [202].

In the United States, various well-established energy recovery techniques are in use including electricity and mechanical energy production, and heat recovery through biogas generated from anaerobic digestion of waste sludge [36]. The use of methane as a source of hydrogen to generate energy with liquefied carbonate fuel has been effectively exhibited at King County, Washington' South treatment plant [203]. Co-digestion of grease (from restaurant trap haulers) with sewage sludge is practicing in Watsonville, California in order to improve the biogas yield by over 50% [204]. Grease comprises the energy rich compounds such as fats, carbohydrates, sugars, etc. [205], thus it is an appropriate substrate for biogas production during anaerobic digestion of sludge. Incinerated sludge ash is used in Columbus, Ohio, as a water-absorbent surface amendment in sports fields and horse arenas [206]. The ash from thermal oxidation installations are used for brick manufacturing by the municipalities of Virginia and Georgia; and as a source of phosphorus by municipality of Cincinnati, Ohio [207]. The dried biosolids products (OCEANGRO™) are used as organic fertilizer by over 60 New Jersey golf courses and registered with the New Jersey Department of Agriculture. Moreover, the biosolids are used as a fertilizer to grow canola (used to make biodiesel fuel) at King County, Washington (Seattle) [36].

In China, biogas harvesting from sewage sludge is a very common way of resource recovery. The annual methane generation from all feedstock including sewage sludge was assessed at 720 million cubic meters [208]. Moreover, the sewage sludge is also used in the manufacturing of bricks and other building material [209]. The Netherland is well known as one of the first countries that employed the phosphorus recovery at full scale [210]. The Netherland has been aimed to replacing 20% of its current phosphate rock consumption by recovered phosphate [67]. Around 32% of sewage sludge generated in Netherlands is currently used in cement industry and power stations [211]. In the UK, a new program for energy recovery has been proposed by the government including the generation of 20% of electricity from renewable sources by 2020 [212]. In 2005, 10.8% and 4.2% of all the UK renewable energy was recovered by combustion and biogas production, respectively. Germany is actively involved in the advancement of novel technologies for phosphorus recovery from sewage sludge, however, four pilot or bench scale technologies have been developed since 2002 [64].

6. Discussions and conclusion

Management of excess sludge is a serious concern, and due to socio-economic and environmental regulation factors, it is a challenging task for the wastewater treatment sector. Conventional sludge disposal methods such as incineration, disposal in landfills, disposal in oceans and land application are already facing increasing pressure and protest from environmental authorities and from the public domain. Thus selection of an efficient and sustainable way for sludge management is a mammoth challenge for wastewater treatment authorities. At the same time, a worldwide hike in fuel prices, rapidly depleting non-renewable resources due to rising demand and supply burden, public awareness as well as climate change issues driven the interest of scientific community to utilize the waste sludge as a valuable resource of renewable energy recovery. The waste sludge was treated in several ways to recover different value added products, viz., energy rich biogas (methane, hydrogen, syngas), liquid bio-fuels (bio-diesel, bio-oils), construction material (bricks, cement, pumice, slag, artificial lightweight aggregates), bio-plastic, proteins and hydrolytic enzymes, bio-fertilizers, bio-sorbent, bio-pesticides, electricity generation using microbial fuel cells, nutrients (nitrogen and phosphorus) and heavy metals. Anaerobic digestion, incineration, pyrolysis, gasification, wet air oxidation, supercritical water oxidation and hydrothermal treatment are the major techniques utilizing worldwide to treat the waste sludge for resource recovery.

Bio-methane recovery by well established anaerobic digestion technique is the main source of energy at a municipal WWTP. Methane is used to producing electrical and thermal energy for on-site use in the treatment plant. However, the slow hydrolysis of waste sludge is the drawback of conventional anaerobic digestion method, which can be overcome by applying the physical, chemical, thermal or mechanical pretreatment step. Nutrient recovery in terms of phosphorus and nitrogen is another way to utilize the fertilizer value of waste sludge. A commercial process named Aqua Reci utilizing SCWO technique showed promising results in phosphate recovery from sewage sludge at pilot scale. Heavy metals (Zn, Cu, Ni, Cd, Pb, Hg and Cr) are the principal elements restricting the use of sludge for land application due to probable soil and ground water contamination, which ultimately affect the human and animal health. A mechanically assisted chemical process (ultrasonication assisted acid leaching) with greater metals recovery has been successfully implemented at industrial scale in a heavy metal recovery plant in Huizhou city, China from more than 2 years. Reuse of waste sludge in production of construction material (bricks, cement, lightweight aggregates) can solve the massive sludge disposal problems. However, the commercialization of sewage sludge based construction material i.e. scale up of technologies and market development is a prerequisite. Environmental friendly liquid and gaseous biofuels (bio-oil, biodiesel, syngas, H_2 gas) recovery from waste sludge is a good alternate to replace the non-renewable petroleum fuels. However, extensive efforts are required in the direction of process optimization for efficient and economic biofuels production from waste sludge. Conversion of waste sludge in electricity generation using microbial fuel cells is an emerging technique, which requires substantial research to scale up this technique in terms of efficient and economic operation. The utilization of waste sludge (using biotechnological approaches) into the production of Bio-plastic, bio-fertilizers, bio-pesticides, protein, hydrolytic enzymes is another area that shows the promising outcomes. However, economically lower yields, infancy stage of recovery methods, lack of substantial research, cost factor, supply chain management are the major factors required major attention in future studies. Table 6 give an overview on the status of the emerging and established technologies used for resource recovery from waste sludge.

Building the sludge derived resources recovery system will help to produce environmentally benign products, reduce the dependency on non-renewable resources thus facilitate the conservation

Table 6
An overview on the status of sludge to resource recovery technologies [36].

Process	Technology		Application Full-Scale	Total energy input (kWh/dr MT)	Total energy output (kWh/dr MT)	End product	Final use
	Type	Status	Number				
Biogas							
Anaerobic digestion	Bioterminator	Emerging	No	N.A.	N.A.	–	N.A.
Thermal hydrolysis	Cambi	Established	>10	0.3	5.97	–	Agriculture
Thermal hydrolysis	BioThelys	Established	2	N.A.	N.A.	–	Disposal
Sludge disintegration	MicroSludge	Established	2-demo	502	1358	–	N.A.
Sludge disintegration	Ultrasonic	Established	9	141	N.A.	–	N.A.
Sludge disintegration	Ozonation	Emerging	No	1923	1736	–	N.A.
Sludge disintegration	Pulse Electric	Emerging	No	N.A.	N.A.	–	N.A.
Syngas							
Gasification	Kopf	Established	1	100	1400	–	Asphalt
Gasification	EBARA	Established	6	N.A.	N.A.	–	Glass granule
Incineration	Thermylis HTFB	Established	1	N.A.	N.A.	–	Ash treatment
Bio-oil							
Pyrolysis	EnerSludge	Established	1	120	1966	–	Brick industry
Pyrolysis	SlurryCarb	Established	1-demo	712	758	–	Fuel in cement
Hydrothermal	STORS	Emerging	No	1394–1410	1480–1898	–	Fuel production
Phosphorus							
KREPO	–	Emerging	1-demo	463	N.A.	Ferric P	Fertilizer only
Seaborne	–	Emerging	1-pilot	N.A.	N.A.	Magnesium ammonium phosphorus	Fertilizer only
Aqua-Reci	–	Emerging	1-demo	738	3167	Calcium P	Phosphate industry
Kemicond™	–	Emerging	1-demo	187.5	N.A.	Ferric P	Fertilizer only
BioCon	–	Emerging	1-pilot	N.A.	N.A.	H_3PO_4	Phosphate industry
SEPHOS	–	Emerging	No	N.A.	N.A.	Calcium P	Phosphate industry
Crystalactor	–	Established	3	N.A.	N.A.	Calcium P	Phosphate industry
Phostrip	–	Established	4	N.A.	N.A.	Calcium P	Phosphate industry
Nitrogen							
ARP	–	Emerging	1-pilot	N.A.	N.A.	Ammonia	Chemical industry
Building material							
Thermal solidification-ALWA	–	Established	>1	1856	N.A.	ALWA	Construction
Thermal solidification-Slag	–	Established	>1	1658	N.A.	Slag	Ceramic
Thermal solidification-Brick	–	Established	>1	2101	N.A.	Brick	Construction
Vitrification-GlassPack	–	Established	1	5715	3626	Glass	Road

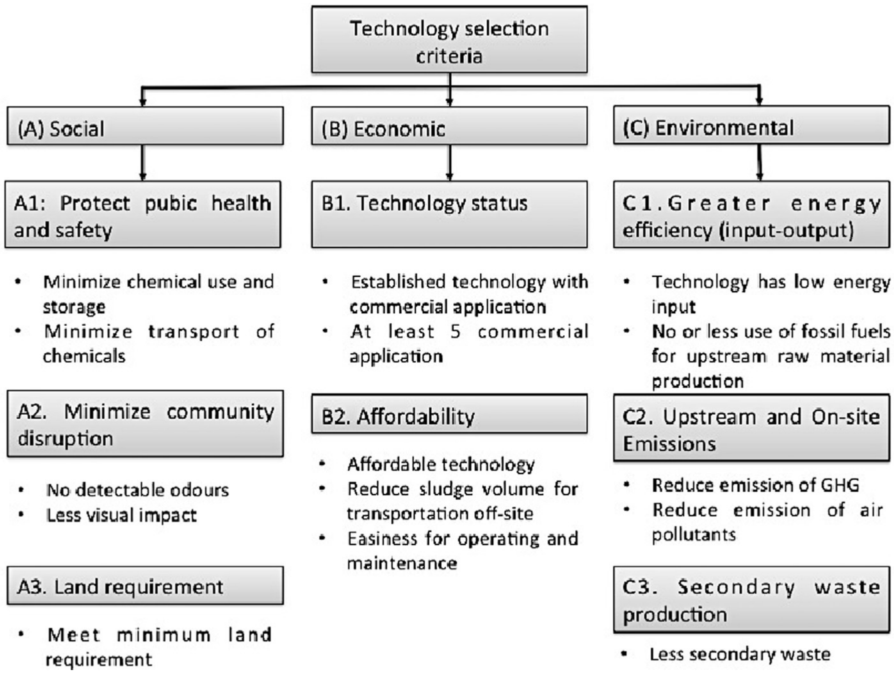

Fig. 5. Social, economic and environmental criteria for related to technology development for resource recovery from waste sludge [36].

of natural resources, decrease the human health risk and environmental pollution (by complete elimination of the pathogens, reducing the risk of soil and ground water contamination from heavy metals and other emerging contaminants associated with landfilling and land application of sludge, reducing the green house gasses emissions associated with burning of petroleum fuels) as well as offers the routes for sustainable management of waste sludge i.e. environmental friendly, economically feasible and socially acceptable (Fig. 5).

Social feasibility is a major issue, as the technology that cannot meet the social acceptance will usually be difficult to find a place in market. The future efforts must also involve the scale up (laboratory-scale to the pilot scale or commercial scale) of sludge to resource conversion techniques, as most of the techniques are only laboratory scale curiosity till now. The cost effective production of value added products with supply chain management and environmental compatibility are another major issues also needs the simultaneous attention during the development of different processes. Several developments have been failed mainly due to the high capital and operation and maintenance cost. The major issue with the resource recovery from waste sludge is related to manufacturing cost of value added products versus the market price [36]. Moreover, the method must generate few or several low-volume and high-value chemical products, as well as low-value and high-volume liquid transportation fuel, while producing electricity and process heat for its own use and possibly adequate for sale of electricity. The high-value products increase profitability, the high-volume fuel support to fulfill national energy demands, and the power generation decreases the costs and sidesteps greenhouse-gas releases [213]. Nevertheless, the success of the sludge-derived resources together with recovery methods will depend mainly upon the technical and economical feasibility, environmental sustainability, marketing facets and public acceptance.

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